Experiments on Film Elasticity and Surface Relaxation[1]

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Abstract

The effect of extensive purification by foaming (and foam removal) upon the surface tension, the Marangoni effect, and upon the film elasticity of solutions of sodium dodecyl sulfate and sulfonate has been studied. Evidence is presented that complete purification was not obtained and that the persistence of a Marangoni effect with a long relaxation time is a sensitive test for surface impurities.

Introduction

THE IMMEDIATE EFFECT of extending a liquid surface containing adsorbed molecules is that the area per adsorbed molecule increases and the surface tension increases. Such behavior and its reverse are often called the Marangoni effect. In the case of an insoluble monolayer, nothing further occurs after the expansion, and surface tension remains constant at the higher value.

If the adsorbed molecules are in equilibrium with those dissolved in the bulk liquid, in general, the original area per molecule will be re-established by replenishment from bulk and the surface tension will then return to the original value. The surface thus relaxes. The time for this relaxation must be of the order of magnitude of the time required for diffusion through a layer of solution which contains the amount of solute required to form a monolayer. The thickness of a compact surfactant monolayer is about 15Å, and the corresponding layer of a solution of 0.1% concentration is 15,000Å (deep); the time for diffusion through this layer is thus in the order of 1μ sec if one assumes a diffusion coefficient of 10^{-5} cm^2/sec. More detailed theories of the process yield similar estimates, and vibrating jet experiments confirm them (1). The relaxation time, being inversely proportional to the square of the concentration of the surfactant, increases rapidly with dilution and approaches a minute for 10^{-3}% solution.

When a thin liquid film (a soap film) is extended, the situation is more complicated. Equilibrium is again re-established between the two surfaces and the intralamelar solution. Because of the minute volume of this solution its concentration is altered significantly by the replenishment of the surfaces, and the *status quo ante* is not completely re-established. The surface tension γ does not return to the original value but to a higher one. Thus the contractile force of a film increases as its area s is increased, and the film exhibits an elasticity modulus E, defined by Gibbs (2) as:

$$E = 2\, d\gamma/(ds/s)$$

If the film is in contact with bulk solution, this first equilibration occurring within the film may be followed by diffusion of solute along the film to restore the original concentration, but this further equilibration is such a slow process that it will be neglected.

The time required for equilibration across a thin film should be of the order of diffusion of surfactant across it, i.e., of the order of microseconds for a film 1 micron thick and diffusion coefficients of the order of 10^{-5} cm^2/sec.

Gibbs' elasticity modulus was first measured only in 1961 by Mysels et al. (3). Their method used the Marangoni effect of a rapidly extended and compressed solution surface to extend and compress a thin film in contact with this solution. The changes in surface tension and in the area of the film were measured directly. The apparatus used will be described below. The times involved in these experiments were of the order of seconds, and concentrations of surfactant exceeded 0.1%. It was therefore clear that the Marangoni effect was caused by additional components and that Gibbs' further analysis of the elasticity of a two-component system (4) was not applicable. Additional evidence cited at the time for the presence of important surface-active contaminants was that the film elasticity modulus was independent of the thickness of the film whereas, in a two-component system, it must increase as the volume of depleted solution decreases, i.e., as the film becomes thinner. As no special effort was made at the time to attain surface purity, these effects were not surprising.

Prolonged foaming of a solution below the critical micelle concentration, combined with continuous removal of the foam, is well known to be an effective method of purifying surfaces (5). It is based on the fact that effective surfactant impurities are by definition those which adsorb at the surface and are present in small amounts so that they may be effectively removed with the foam before the main component is excessively depleted. The effectiveness of the method with respect to known and unknown contaminants has been recently demonstrated in this laboratory for solutions of sodium dodecyl sulfate (6).

The original purpose of the present work was to investigate the effect of surface purification by foaming in the above method of measuring surface elasticity in order to see how far the method was applicable and whether the expected effect of film thickness upon elasticity could be detected. The results to be reported have lost some of their significance since Prins et al. (7) have in the meantime simplified the method of measuring Gibbs' film elasticity by eliminating the need for the Marangoni effect. They depend upon the weight of the additional film pulled out of the solution to stretch the observed film. In addition however, the present study shows that the Marangoni effect is an extremely sensitive test for surfactant impurities and that even extensive foaming may not guarantee the presence of a pure surface.

Experimental Procedures

The apparatus (Fig. 1) was based on the one already described (3), which consisted of a square glass bottle with a 5 × 5cm inner cross-section made from precision-bore glass with two adjacent walls optically polished on their outside surfaces, through which the film was illuminated and photographed. The top of

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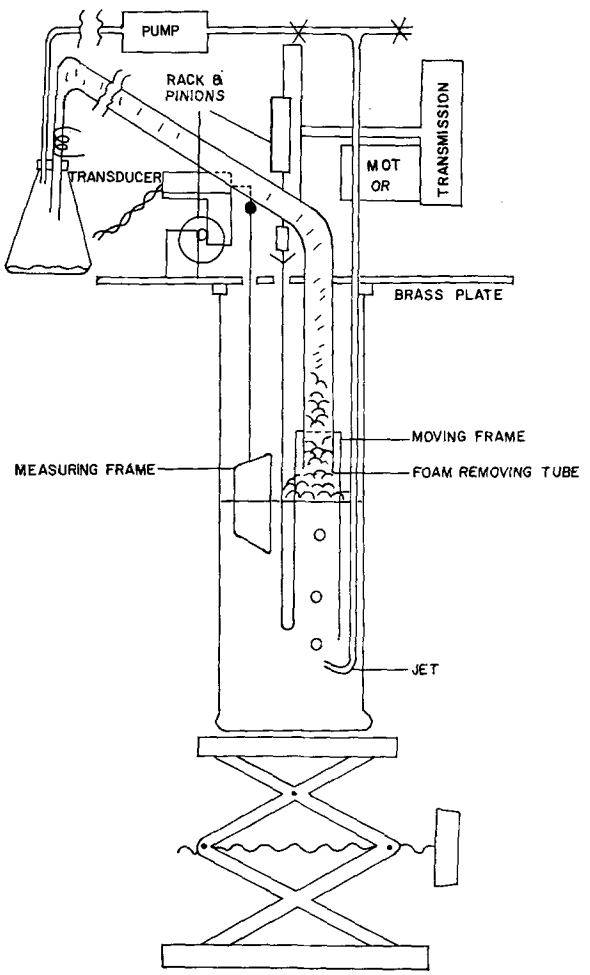

FIG. 1. Schematic diagram of the apparatus used. One of the moving frames is not shown, and the foam-breaking part is disproportionately reduced. The distortion of the measuring frame indicates its orientation at 45° to the plane of the figure.

the bottle was attached to a brass plate, through which the other operations and measurements were performed. A variable-speed motorized rack and pinion system operated a film-forming frame, the up-and-down motion of which permitted the rapid extension and contraction of the original 25cm² surface by about 80% and production of the Marangoni effect. A second frame (not shown), carrying no film, moved in unison but in the opposite direction to compensate for buoyancy effects produced by the first one. A sensitive strain-gauge transducer supported a light frame which measured the surface tension and carried the film whose extension was observed. The film was formed by lowering and raising the transducer by means of another small rack and pinion, thereby dipping the light frame in, and then withdrawing it from, the liquid. The electric signal from the transducer was amplified and recorded, and the motion of the fringes of the film was registerd by means of a slit camera.

The main change in adapting the apparatus for the present work was the addition of a foaming system similar to the one used by Elworthy and Mysels (6). This system consisted of a thin tube terminating in a jet within the liquid, through which air bubbles were injected, and a wide tube above the surface, followed by an inclined section through which the foam thus formed was aspirated and in which it drained so as to reduce the loss of solution. Most of the air was recirculated with a modified aquarium pump after the foam was broken by heating.

In addition, various precautions were taken against possible contamination of the surface, e.g., the brass plate was coated with a vinyl film and further protected by a Teflon shield; the glass parts of the frame-supporting rods were extended above the brass plate, and Teflon collars were placed on them to protect the openings in the plate. As a result, the properties of purified surfaces showed no significant changes over periods of 24 hrs or longer when not subject to foaming.

Forces exerted upon the frame in the absence of a film were practically eliminated by carefully adjusting the relative positions of the moving frames to balance the hydrodynamic effects within the solution.

The displacement of fringes as the film expands and contracts was measured with increased precision directly on the photographic film by using a vertical traveling microscope. The crosshair was first set at an angle and height to coincide with two neighboring crests, and then the microscope was lowered until the crosshair coincided with the intermediate trough. Several such measurements were combined, as described earlier (3), to give a measure of the relative extension of the film.

The principal uncertainty in measuring the film elasticity modulus was in the determination of ds/s. After some experience, results obtained by duplicate analysis of the same photographic record agreed to 0.003, and those of different films were measured under the same conditions, generally to 10% or 0.003, whichever was larger. In a few cases however these limits were significantly exceeded for no apparent reason.

Evaporation within the bottle was reduced as far as possible by a good gasketing between the bottle and the plate and by enclosing all of the equipment mounted on top of the plate in a polyethylene bag along with Petri dishes containing some water. Nevertheless film stability was not satisfactory for long-term studies, and, in later work, the frames were replaced by wetted plates. First, sandpapered platinum was used, then cover glasses sealed to a Corning-7530-glass fiber.

The concentration of the solution, which was slightly changed by the foaming, was determined when required by measurement of its electric conductivity in a separate cell.

The sodium dodecyl sulfate samples were previously prepared from high purity alcohol and conventionally purified in this laboratory. The sodium dodecyl sulfonate was a carefully purified sample, showing no surface tension minimum, which was donated by E. D. Goddard of the Lever Brothers Research Center.

Results

As expected, purification by foaming (or, briefly, foaming) increased the surface tension of the solutions markedly in the early stages. After this the increase was not significantly different from that expected from the slight change of concentration which was caused by removal of surfactant with the foam. The Marangoni effect measured by the change in the surface tension, $\Delta\ \gamma$, produced by an 80% extension of the surface, also decreased markedly at first, then more slowly, but was not eliminated. Film elasticity decreased somewhat at first, then remained quite constant. These effects are shown in Fig. 2 for a solution of NaLS. The effect of concentration below the critical micelle concentration (cmc) upon the film elasticity

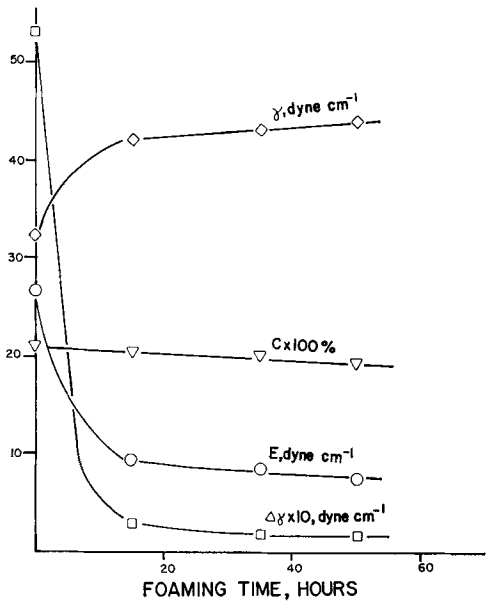

FIG. 2. The effect of purification by foaming upon a 0.21% solution of sodium dodecyl sulfate at 23C upon its concentration C, its surface tension γ, its Marangoni effect upon 80% extension of the surface $\Delta\ \gamma$, and its film elasticity modulus E.

of purified solutions was small. The modulus of elasticity obtained was about 8.8 dyne/cm at 0.9%, 7.5 at .19%, whereas above the cmc 1.1 dyne/cm at .35% was obtained.

The constancy of the elasticity upon prolonged foaming (Fig. 2) could suggest that a limiting value which was valid for a pure system was obtained. Several observation oppose this conclusion however. One is the persistence of the Marangoni effect. Another is that the film elasticity modulus, which sometimes increased as the film thickness decreased in less purified systems, always became independent of thickness as purification proceeded. This effect is shown in Fig. 3 in terms of total extension for two films, the curvature of which gives the variation of the modulus. As mentioned above, Gibbs' theory requires a thickness dependence for a two-component system. Finally, the fact that the relaxation time of the Marangoni effect was of the order of minutes proved that surface behavior did not approach that expected of a pure surface.

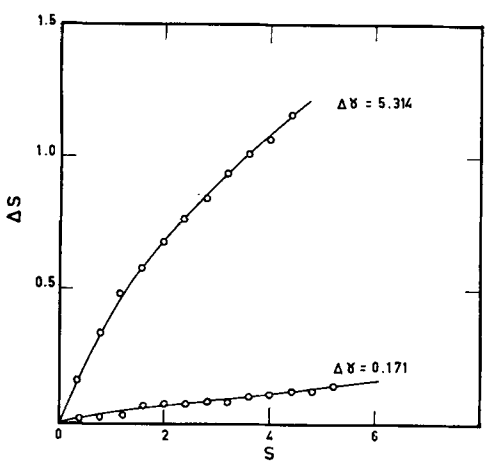

FIG. 3. Typical extension of a film upon the indicated increase in surface tension $\Delta\ \gamma$, as a function of distance from the top of the film, before (upper line) and after (lower line) extensive foaming. For each line the modulus is proportional to the slope at each point.

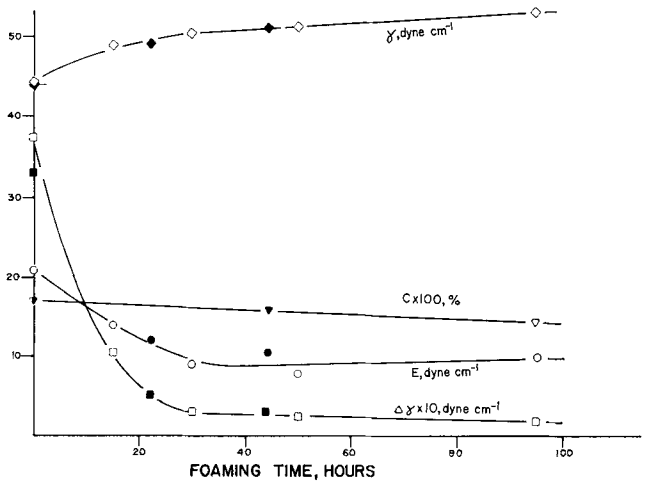

FIG. 4. The effect of purification by foaming upon a 0.17% solution of sodium dodecyl sulfonate at 23° upon its concentration C, its surface tension γ, its Marangoni effect upon 80% extension of the surface $\Delta\ \gamma$, and its film elasticity modulus E.

This failure of foaming to purify the solution suggested that impurities are being produced continuously in the system so that a steady state is attained when the rates of removal and production are equal. The most likely source of such continuously produced impurity seemed to be the possible hydrolysis of the dodecyl sulfate ion to give dodecyl alcohol and sulfuric acid. Such hydrolysis has been reported (8) although it has never been found significant in this laboratory. To eliminate the possibility of such complications because of hydrolysis, the experiments were repeated by using the corresponding sulfonate. As shown in Fig. 4, the results were however essentially the same and quite reproducible, thus eliminating this particular explanation. (The elasticity modulus measured was about 6.5 dyne/cm at .09%, 9.8 at .143%, and 10.5 at .157%.)

As the most striking anomaly was the long relaxation time of the Marangoni effect, it was decided to investigate it further in a simplified system, in which films were replaced by plates to avoid the disturbing effects of bursting. Glass proved to be somewhat better wetted than sandpaper-depolished and ignited platinum. (Subsequent experience indicates that sandblasting gives a much more wettable platinum surface than depolishing with sandpaper and that ignition

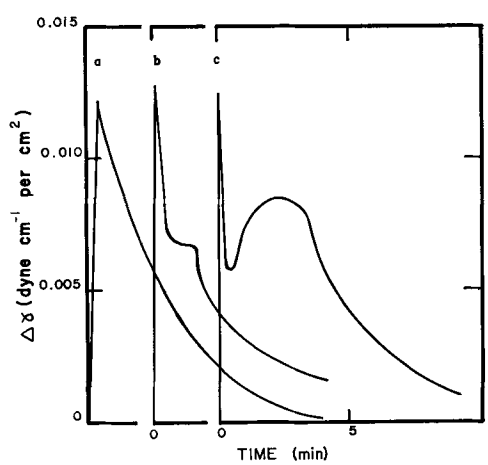

FIG. 5. The effect of rate of extension upon the course of relaxation of surface tension. Extension by about 90% of the horizontal surface: a in 22 sec, b in 5.5 sec., c in 2.2 sec. Glass plates used for both extension and sensing.

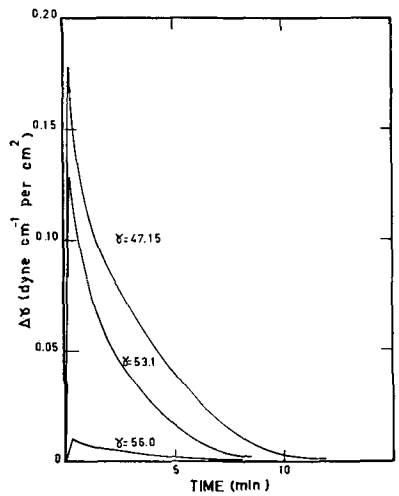

FIG. 6. Typical effect of foam purification upon the extent of the Marangoni effect and upon its relaxation. Sodium dodecyl sulfonate 0.1% at 23C, slow rate of extension by about 90%. Upper curve before foaming, middle curve after 4 hrs of foaming, lower curve after 15 hrs of foaming. Relaxation occurs at about the same rate despite large differences in $\Delta\ \gamma$.

reduces wettability as found by Boucher, Grinchuck, and Zettlemoyer (9)).

Many variations of the experimental conditions were attempted. An interesting incidental observation was that, when a plate was rapidly raised, the surface tension of the solution went through a minimum and a maximum during its return to the equilibrium value as shown in Fig. 5. This figure also shows that the effect was absent after a slow raising of the plate and led to a hump at intermediate rates. The probable explanation is that, during rapid raising, the plate entrains a significant layer of the solution by purely viscous forces. Once the plate is stopped, this layer flows down and in the process stretches its outer surface and carries some of the adsorbed surfactant down to the bulk surface, causing the observed minimum. As this downward flow ebbs, the stretched surface shrinks and some surfactant is again removed from the bulk surface, giving rise to the maximum. It should be noted that these are small effects measured in thousandths of a dyne/cm and would normally be overlooked.

Despite many variations of the experimental conditions to ensure the absence of contamination and to improve the purification procedure, the result with respect to the Marangoni effect remained unchanged. The extent of the Marangoni effect, i.e., $\Delta\ \gamma$, could be greatly reduced by foaming but only to a limiting value and its relaxation time was always about the same. Fig. 6 shows a typical result.

The authors have no explanation to offer at this time. The complicated apparatus placed certain limitations upon procedures, and it is not possible to assert that significant contamination was absent. Experience indicates however that either an unexpected new type of surface behavior has been encountered or that extended purification by foaming and a constancy of surface tension and of film elasticity during that procedure are not by themselves guarantees of real surface purity.

It should be emphasized that the Marangoni effect is a simple and sensitive test of the conditions of a surface, one which provides considerable information in addition to that obtainable from a measurement of the equilibrium surface tension.

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